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(54) Title: IMPROVEMENTS IN OR RELATING TO FILMS

(57) Abstract: A low gas barrier, multi-layer film; and a medium gas barrier, multi-layer film, a high gas barrier, multi-layer film; and a relatively elastic, multi-layer film are suitable for use on a pouch-producing, vertical, form-fill-seal machine. At least the majority of the layers may be bonded together through their having been co-extruded. The outermost layer, which may be PP, can be manufactured by extrusion to form a fist sub-film which is later laminated to the other layers of the film, which have been co-extruded to form a second sub-film. Wen the second sub-film is to provide a significant barrier to gas, particularly oxygen, it can consist of a PA; PA/EVOH/PA; EVOH; PA/EVOH; PVDC; or PA/aromatic PA/PA; 1-to-3-layer core sandwiched between two EVA-, EMA-, PP-, HDPE-, LLDPE-, POP- or LDPE- based adhesive layers, sandwiched between an outermost layer of PO, polyester, PP, or PC, and an innermost sealing layer of PO, polyester, PP, or PC, and an innermost sealing layer based on Pos (mainly) polymerized using a single site catalyst system, the layers being pigmented in such a way that an effective barrier against visible light is created. The layers of the second sub-film may be doubled by collapsed bubble co-extrusion.

IMPROVEMENTS IN OR RELATING TO FILMS

This invention relates to a multi-layer film, in particular a multi-layer packaging film for use in producing pouches.

Vertical form-fill-seal machines are known for producing plastics pouches filled with a product, often a liquid product, for example a water-containing product such as milk, fruit juice, sauce or wine, or water itself. It is an object of the present invention to provide a multi-layer film which is especially suitable for use on such machines and for protecting the packaged product against deterioration or escape.

WO-A-97/02948 discloses a film applicable in particular for fabricating pouches for packaging flowable or pumpable, liquid, pasty or solid goods which goods are light sensitive, e.g. milk. The film has e.g. five layers of which the inside layers perform the function of the light barrier and the function of colouring the material and contain e.g. black, white pigments, whereas one of the surface layers serves as a sealing layer and contains no pigment or a very low concentration of white pigment and the other surface layer serves as a printing layer and contains advantageously calcium carbonate which renders the layer readily printable. A five-layer example of the film, progressing outwardly, consists of low density polyethylene (LDPE) containing titanium dioxide (TiO_2)/adhesive containing TiO_2/polypropylene (PP) containing carbon black/adhesive containing TiO_2/LDPE containing calcium carbonate ($CaCO_3$). Further examples may omit the fourth, fifth and/or second layers and/or introduce further layers such as ethylene vinyl alcohol (EVOH).

JP-A-10-100346 discloses a co-extruded film suitable for a food packaging bag and consisting of a layer having as a component polyamide (PA), polyester or a propylene polymer and another layer having a blend of an alpha-olefin co-

polymer and a polymer produced by graft polymerization of an unsaturated carboxylic acid or a derivative thereof. Thus, the use of one or more separate, dedicated, adhesive layers is avoided.

EP-A-0545649 discloses a multi-layer polymeric film consisting of a core layer of a polyolefin (PO) containing a light-absorbing pigment, an intermediate layer on each surface of the core layer, each intermediate layer consisting of a PO and a pigment and/or a voiding agent, and an outer layer of a heat-sealable polymer on each outer surface of the intermediate layers. In one example, a flat five-layer polymer web was produced by co-extruding through a slot die a central core layer of propylene homopolymer containing carbon black (average particle size less than 0.2 micron), intermediate layers of the same propylene homopolymer as the core layer but without the carbon black on either side of the core layer, and an a layer of a propylene/ethylene copolymer on each intermediate layer, one of the outer layers containing TiO_2 (average particle size less than 0.2micron). The resulting web was then biaxially oriented to create voids therein. In another example, the two intermediate layers each contained TiO_2. Such films had a high degree of light barrier and low water vapour transmission rates.

According to one aspect of the present invention, there is provided a multi-layer packaging film comprising, progressing towards a surface of the film intended to contact a product to be packaged, an outermost layer, an intermediate layer, and a product-contacting layer, at least one of the layers being of a material the stiffness of which decreases following contact with a constituent of said product, the arrangement being such that said material is able to come into contact with said constituent after said product has been packaged in said film.

Preferably, at least one of the product-contacting layer and the intermediate layer is of such a material.

Advantageously, the product to be packaged is aqueous and the material is one, particularly PA, the stiffness of which decreases following contact with moisture, the film, from its product-contacting surface to said material, being moisture-permeable.

Owing to this aspect of the invention, it is possible to provide a multi-layer film which has enough stiffness to give good machine-friendliness as regards its running through the machine, on pouch-producing, form-fill-seal machines and which nevertheless acquires good impact-and drop-strength after filling with the product.

If the outermost layer has a higher softening point than the product-contacting layer, the machine friendliness of the film as regards its sealability is improved.

According to another aspect of the present invention, there is provided a multi-layer packaging pouch comprising, progressing towards a surface of the pouch contacting an aqueous product packaged therein, an outermost layer, an intermediate layer, and a product-contacting layer, said outermost layer having a higher softening point than said product-contacting layer, and said intermediate layer comprising a material having a higher drop strength than the material of said outermost layer.

Owing to this aspect of the invention, seals of the pouch are less likely to break than if the intermediate layer were to have a lower or equal drop strength, because the intermediate layer acts as a better absorber of shocks.

If desired, at least one of the intermediate layer and the product-contacting layer may have a higher light barrier property than the outermost layer.

For the film to be machine-friendly, at least one of the outermost layer and the intermediate layer should be of a material stiffer than that of the layer which will contact the product. For this reason, the outer layer may comprise a stiff, extrudable polymer, for example polyester -

especially polyethylene terephthalate (PET)-; PP (especially crystalline PP); polycarbonate (PC); or high density polyethylene (HDPE); although PP is preferred.

Again, for the film to be machine-friendly, the outermost layer and the innermost (i.e. product-contacting) layer should have a significant melting point differential of at least 15°C as measured by Differential Scanning Calorimetry (DSC), preferably of at least 25°C, but particularly of at least 40°C, so that the outermost layer does not soften when the innermost layer is sealed (it being understood, of course, that the innermost layer is heat-and pressure-sealed to itself in the forming of a pouch). Materials giving a high softening point for the outermost layer would be stiff, possibly crystalline, resins such as PET, PP, PC and HDPE, although PP is preferred.

Further, for the film to be machine-friendly, the innermost and outermost layers preferably include antiblock and slip compounds, for example silica and erucamide acid.

For the film to protect the packaged product against escape, the aforementioned intermediate layer (of which there may be a plurality) has good (impact - and) drop-strength, for which reason one or more highly flexible and possibly amorphous resins in the form of polymers would be employed. Such polymers are impact-modified PPs, including those produced using metallocene-type catalyst systems, LDPE, m-LDPE (i.e. LDPE made by using a metallocene catalyst system) (with densities as low as 0.88 g/cm^3), particularly where the product is food; for other products additionally very low density linear low density polyethylene (VLLDPE), particularly VLLDPE polymerized using a Ziegler Natta catalyst system and, after polymerization, grafted with maleic acid anhydride (MAH) (i.e. MAH-mod-VLLDPE); polyolefin plastomer (POP), especially POP made by using a metallocene catalyst system (m-POP); and PA with a low degree of crystallinity, particularly a copolyamide, especially one

copolymerized by condensation polymerization of a diamine and a dicarbonic acid. Advantageously, the innermost layer should also have good (impact - and) drop-strength, so that at least one of such polymers would again be employed in the innermost layer.

For the film to protect the packaged product against both deterioration and escape, good sealing properties (in particular a good hot-tack property), even through a wide range of liquid products, and low taste induction can be obtained in the innermost layer by the use of one or more high-performance resins with a very low level of short molecular weight fractions and an ultra low level of non-polymerized monomers. Such resins may be low softening point, flexible polyolefins. Usable are one or more of LDPE; m-LLDPE; and m-POP.

Again, for the film to protect the packaged product against deterioration, at least one of the intermediate layer and the innermost layer may constitute a barrier to visible light. Advantageously, at least one barrier is dark, preferably black, in colour and at least another barrier is light, preferably white, in colour. It is particularly advantageous if there are an innermost light barrier and an outermost light barrier which are light, preferably white, in colour and at least one intermediate light barrier which is dark, preferably black, in colour. In this way, it is possible to obtain virtually 100% (at least 99.9%) protection against visible light, whilst also obtaining an aesthetically pleasing appearance. The barriers can be obtained by pigmentation of appropriate layers, for example with carbon black and TiO_2.

Thus, according to another aspect of the present invention, there is provided a multi-layer film comprising:-

a first layer comprised of any of the group consisting of PET, PP, PC and HDPE,

a second layer comprised of a sealing polymer,

between said first layer and said second layer, third and fourth layers of which the third layer is nearer to said first layer than is said fourth layer,

light-coloured pigment in said third layer,

dark-coloured pigment in said fourth layer, and

light-coloured pigment in said film and located between said dark-coloured pigment and that surface of said film further from said first layer.

The sealing polymer is preferably produced using a metallocene catalyst.

Owing to this aspect of the invention, because of the melting point differential between the first and second layers, good seal strength is achievable, especially through product or contamination, so that a film constituting a good light barrier and partularly suitable for use on a pouch form-fill-seal machine can be obtained.

According to a further aspect of the present invention, there is provided a method of producing a laminate by collapsed bubble extrusion, comprising extruding a multi-layer tube including a light-barrier substance, and collapsing the tube and thermo-laminating the innermost layer of the tube to itself.

According to a yet further aspect of the present invention, there is provided a laminate in the form of a collapsed, multi-layer tube which includes a light-barrier substance and whereof the innermost layer is in a condition thermo-laminated to itself.

Owing to these two aspects of the invention, it is possible to obtain a laminate which, for the same proportion of light-barrier substance, is a more effective light barrier than a laminate produced by a conventional blown film system. We believe that this is because the light barrier substance is split up in two flat layers rather than being in a single flat layer. Moreover, compared with a film produced by a conventional blown film system, it is easier to avoid having the light barrier substance at a surface of a relatively thin

laminate. Furthermore, the feature of collapsed bubble extrusion, whereby the collapsed bubble passes between hot nip rollers has not only the effect of evening out the thickness of the laminate, but also of evening out the distribution of the light barrier substance.

The production of the laminate may be followed by forming a section of the laminate into a container by bringing and sealing together opposite edge zones of the section to give the section a tubular form, sealingly closing a lower end of the tubular-form section, filling the tubular-form section with a product, and then sealingly closing the upper end of the tubular-form section. If the laminate is in the form of a film, a pouch can be produced in this way.

When a gas barrier laminate is required, one or more further intermediate layers having gas barrier properties may be included. The gas barrier is advantageously effective against the transmission of oxygen, carbon dioxide and nitrogen, particularly oxygen. The gas barrier is provided by aluminium (Al), aluminium oxide (Al_2O_x), silicon oxide (SiO_x), melamine, diamond-like carbon, or one or more polymers, for example EVOH; polyvinylalchohol (PVOH); polyvinylidene chloride (PVDC); or PA.

In order that the film may be relatively inexpensive to produce, it is advantageous to bond at least the majority of the layers together through their having been co-extruded (rather than their having been laminated together as respective films). Such co-extrusion can be cast (through a slot die) or blown co-extrusion. If desired, the outermost layer, which may be PP, can be manufactured by cast extrusion (where it is a single stratum) or co-extrusion (where it consists of a plurality of strata) to form a first sub-film which is later laminated to the other layers of the film, which have advantageously been co-extruded to form a second sub-film. To promote bonding to the second sub-film, the inner surface of the outermost layer can be appropriately

treated, for example by corona discharge, or by applying one or more primers, before lamination. If desired, the treated, inner surface can be printed with artwork prior to lamination. When the second sub-film is to provide a significant barrier to gas, particularly oxygen, it can be made by a cast or blown co-extrusion method and consist of a PA; PA/EVOH/PA; EVOH; PA/EVOH; PVDC; or PA/aromatic PA/PA; 1-to-3-layer core sandwiched between two ethylene vinyl acetate (EVA-), ethylene methacrylic acid (EMA-), PP-, HDPE-, linear low density polyethylene (LLDPE)-, POP- or LDPE- based adhesive layers, sandwiched between an outermost layer of polyolefin (PO) (for example polyethylene-PE-), polyester (for example PET), PP, or PC, and an innermost sealing layer based on POs (mainly) polymerized using a single site catalyst system, the layers being pigmented in such a way that an effective barrier against visible light is created.

If the film is to be relatively elastic at least at its outer surface, its outermost layer may comprise a rubber-modified plastics. However, the film should still have a relatively large melting point differential of its outer surface over its inner surface in which case the rubber-modified plastics needs to have a relatively high melting point. Such plastics may be PP, PET, HDPE, or PC. In those circumstances, the film may be produced by co-extrusion without any lamination.

In order that the invention may be clearly and completely disclosed, four examples thereof will now be described with reference to the accompanying drawings, in which Figures 1 to 4 are respective, diagrammatic, fragmentary cross-sections through a low gas barrier, multi-layer film; a medium gas barrier, multi-layer film; a high gas barrier, multi-layer film; and a relatively elastic, multi-layer film, respectively, suitable for use on a pouch-producing, vertical, form-fill-seal machine; whilst Figures 5 to 7 illustrate diagrammatically, in fragmentary cross-

sections, the manufacture of sub-films of a low gas barrier multi-layer film; a medium gas barrier multi-layer film; and a high gas barrier multi-layer film, respectively.

Referring to the drawings, the film of Figure 1 consists of the layers 2 to 8, that of Figure 2 consists of the layers 10 to 20, and that of Figure 3 consists of the layers 22 to 36. The main constituents, the range of possible thickness, the preferred thickness, and the main properties of each layer are given in the Tables I to IV hereinafter.

In manufacture of the film of each of Figures 1 to 3, the outermost layer 2, 10, or 22, as the case may be, is produced by cast extrusion to form a stiffening sub-film, whilst the other layers 4 to 8, 12 to 20, or 24 to 36, are produced by blown or cast co-extrusion to form a second sub-film which, after bond-enhancing treatment of the inner surface of the stiffening film, and flexographic and/or rotogravure printing of artwork on that surface, is laminated by a suitable adhesive 3, 11, or 23, to the stiffening sub-film to provide the film of the Figure. The adhesive may be, for example, polymethane (PUR), EMA, or an ionomer.

In manufacture of the film of Figure 4, the layers 38 to 46 are produced by blown or cast co-extrusion.

Referring to Figure 5, this shows the manufacture of the second sub-film by a collapsed bubble system in which the blown tube 50 is collapsed to between a pair of hot nip rollers (not shown) to thermo-laminate to itself the innermost layer of the tube 50 to produce the multi-layer sub-film 52 suitable for use on a pouch-producing, vertical, form-fill-seal machine. The tube 50 consists, progressing from the outside to the inside thereof, of a sealing layer 54 of LDPE, m-LDPE, or m-POP; an intermediate layer 56 of PE; and an innermost layer 58 of POP, EVA, EMA, ethylene acrylic acid (EAA), an ionomer, or a polyamide co-polymer with a melting point no higher than about 160°C. Thus, the sub-film 52, which is intended to be laminated to a first film of PP,

PET, PC, or HDPE by a suitable adhesive, consists of those layers 54 to 58 in a doubled form 54' to 58'.

Referring to Figure 6, this shows the manufacture of the second sub-film by a collapsed bubble system in which the blown tube 60 is collapsed to between a pair of hot nip rollers (not shown) to thermo-laminate to itself the innermost layer of the tube 60 to produce the multi-layer sub-film 62 suitable for use on a pouch-producing, vertical, form-fill-seal machine. The tube 60 consists, progressing from the outside to the inside thereof, of a sealing layer 64 of LDPE, m-LDPE, or m-POP; a tie layer 66 of MAH-mod-VLLDPE, or LDPE; an intermediate layer 68 of PA; a tie layer 70 of MAH-mod-VLLDPE, or LDPE; and an innermost layer 72 of POP, EVA, EMA, EAA, an ionomer, or a polyamide co-polymer with a melting point no higher than about 160°C. Thus, the sub-film 62, which is intended to be laminated to a first film of PP, PET, PC, or HDPE by a suitable adhesive, consists of those layers 64 to 72 in a doubled form 64' to 72'.

Referring to Figure 7, this shows the manufacture of the second sub-film by a collapsed bubble system in which the blown tube 80 is collapsed to between a pair of hot nip rollers (not shown) to thermo-laminate to itself the innermost layer of the tube 80 to produce the multi-layer sub-film 82 suitable for use on a pouch-producing, vertical, form-fill-seal machine. The tube 80 consists, progressing from the outside to the inside thereof, of a sealing layer 84 of LDPE, m-LDPE, or m-POP; a tie layer 86 of MAH-mod-VLLDPE, or LDPE; an intermediate layer 88 of PA; a gas barrier layer 90 of EVOH, PVOH or PVDC; another intermediate layer 92 of PA; a tie layer 94 of MAH-mod-VLLDPE, or LDPE; and an innermost layer 96 of POP, EVA, EMA, EAA, an ionomer, or a polyamide co-polymer with a melting point no higher than about 160°C. Thus, the sub-film 82, which is intended to be laminated to a first film of PP, PET, PC, or HDPE by a suitable adhesive, consists of those layers 84 to 96 in a doubled form 84' to 96'.

We believe that the doubling of the layers as in Figures 5 to 7 has the effect of enhancing the desired properties of the laminate compared with the same total thicknesses of individual layer compositions in a non-doubled laminate, in particular of the light barrier properties when, for example, white pigment is included in one or more outer layers of the tube 50, 60, or 80, and black pigment is included in one or more inner layers of the tube 50, 60, or 80.

Although the film of any one of the Figures may be used for packaging various products, especially liquid products such as milk, fruit juice, sauce, wine or water, it is particularly intended for the packaging of milk, which is one of the reasons why the white pigment is used to give the inside and the outside of the film a white colour. The film is also particularly suitable for aseptic or sterile packaging, in being constructed so as to cope with high-pressure steam and hydrogen peroxide employed to maintain aseptic or sterile packaging conditions. The film should be resistant, both inside and outside, to a 35% hydrogen peroxide solution at 60°C for a minimum of 72 hours. 12 to 24 hours after filling with a water-containing liquid food product, the film should show a substantial increase in Dart Drop resistance (according to American Standard Testing Method D1709-1, method B) measured on the film.

When packaging milk and other water-containing products, the film of Figure 2, 3, 4, 6 or 7, has the advantage that the walls of a pouch formed therefrom decrease in stiffness following filling with the product, so that the film is not only machine-friendly but later becomes more (impact- and) drop-resistant.

The film of any one of the Figures is inexpensive, has high machine friendliness on aseptic, form-fill-seal machines (in particular the ELOPOUCH™ E-P4000 Aseptic vertical machine manufactured by Robert Bosch GmbH and available from the Elopak Group of Companies) using high pressure steam and hydrogen peroxide for maintaining sterile packaging

conditions, has superior heat- and pressure-sealing properties through a wide range of liquid products such as milk, fruit juice, water and sauce, with no, or extremely low, off-taste induction in the product, and has excellent recycling properties and can be used in producing pouches with virtually 100% barrier to visible light and with high impact strength and, for the film of Figure 2, 3, 4, 6 or 7, with an effective barrier against oxygen, carbon dioxide and nitrogen gases.

TABLE I

LAYER NO.	MAIN CONSTITUENTS	THICKNESS RANGE (MICRONS) *	PREFERRED THICKNESS (MICRONS)	MAIN PROPERTIES
Low-Barrier Film				
2	PP; Antiblock and Slip Compounds	15 to 60	30	High Softening Point; Machine Friendliness (Stiffness)
4	m-LLDPE; LDPE; White Pigment	15 to 60	30	Light Barrier; Impact-and Drop- Strength
6	Impact-modified PP; Black Pigment	10 to 40	20	Impact-and Drop- Strength; Light Barrier
8	m-LLDPE; m-POP; LDPE; White Pigment; Antiblock and Slip Compounds	15 to 60	30	Impact-and Drop- Strength; Low Softening Point; Light Barrier; Sealability

TABLE II

LAYER NO.	MAIN CONSTITUENTS	THICKNESS RANGE (MICRONS) *	PREFERRED THICKNESS (MICRONS)	MAIN PROPERTIES
Medium-Barrier Film				
10	PP; Antiblock and Slip Compounds	15 to 60	30	High Softening Point; Machine Friendliness (Stiffness)
12	m-LLDPE; LDPE; White Pigment	15 to 60	30	Light Barrier; Impact-and Drop- Strength
14	MAH-mod-VLLDPE; LDPE; Black Pigment	2 to 10	5	Light Barrier; Impact-and Drop- Strength
16	PA	3 to 20	10	Impact-and Drop- Strength; Oxygen Barrier; Stiffness
18	MAH-mod-VLLDPE; LDPE; Black Pigment	2 to 10	5	Light Barrier; Impact-and Drop- Strength
20	m-LLDPE; m-POP; LDPE; White Pigment; Antiblock and Slip Compounds	15 to 60	30	Impact-and Drop- Strength; Low Softening Point; Light Barrier; Sealability

TABLE III

LAYER NO.	MAIN CONSTITUENTS	THICKNESS RANGE (MICRONS) *	PREFERRED THICKNESS (MICRONS)	MAIN PROPERTIES
High-Barrier Film				
22	PP; Antiblock and Slip Compounds	7 to 30	15	High Softening Point; Machine Friendliness (Stiffness)
24	m-LLDPE; m-POP; LDPE; White Pigment	20 to 80	40	Light Barrier; Impact-and Drop- Strength
26	MAH-mod-VLLDPE; LDPE; Black Pigment	2 to 10	5	Light Barrier; Impact-and Drop- Strength
28	PA	2 to 10	5	Impact-and Drop- Strength; Oxygen Barrier; Stiffness
30	EVOH	2 to 10	5	Oxygen Barrier
32	PA	2 to 10	5	Impact-and Drop- Strength; Oxygen Barrier; Stiffness
34	MAH-mod-VLLDPE; LDPE; Black Pigment	2 to 10	5	Light Barrier;Impact-and Drop- Strength
36	m-LLDPE; m-POP; LDPE; White Pigment; Antiblock and Slip Compounds	20 to 80	40	Impact-and Drop- Strength; Low Softening Point; Light Barrier; Sealability

TABLE IV

LAYER NO.	MAIN CONSTITUENTS	THICKNESS RANGE (MICRONS) *	PREFERRED THICKNESS (MICRONS)	MAIN PROPERTIES
Relatively Elastic Film				
38	Rubber-Modified PP; White Pigment; Antiblock and Slip Compounds	25 to 100	50	Light Barrier; Elasticity; High Softening Point;
40	MAH-mod-POP; LDPE; Black Pigment	2 to 10	5	Light Barrier; Impact-and Drop- Strength
42	PA	3 to 20	10	Impact-and Drop- Strength; Oxygen Barrier; Stiffness
44	MAH-mod-POP; LDPE; Black Pigment	2 to 10	5	Light Barrier; Impact-and Drop- Strength
46	m-LLDPE; LDPE; White Pigment; Antiblock and Slip Compounds	35 to 140	70	Impact-and Drop- Strength; Low Softening Point; Light Barrier; Sealability

CLAIMS

1. A multi-layer packaging film comprising, progressing towards a surface of the film intended to contact a product to be packaged, an outermost layer, an intermediate layer, and a product-contacting layer, at least one of the layers being of a material the stiffness of which decreases following contact with a constituent of said product, the arrangement being such that said material is able to come into contact with said constituent after said product has been packaged in said film.

2. A film according to claim 1, wherein at least one of the product-contacting layer and the intermediate layer is of said material.

3. A film according to claim 1 or 2, wherein said material is one the stiffness of which decreases following contact with moisture, the film, from its product-contacting surface to said material, being moisture-permeable.

4. A film according to claim 3, wherein said material is polyamide.

5. A film according to any preceding claim, wherein at least one of the outermost layer and the intermediate layer is of a material stiffer than that of the product-contacting layer.

6. A film according to claim 5, wherein said material stiffer than that of the product-contacting layer comprises a stiff, extrudable polymer.

7. A film according to claim 6, wherein said material stiffer than that of the product-contacting layer comprises polyester, polypropylene, polycarbonate, or high density polyethylene.

8. A film according to claim 7, wherein said polyester comprises polyethylene terephthalate.

9. A film according to claim 7 or 8, wherein said polypropylene comprises crystalline polypropylene.

10. A film according to any preceding claim, wherein the outermost layer has a higher softening point than the product-contacting layer.

11. A film according to claim 10, wherein the outermost layer and the product-contacting layer have a melting point differential of at least 15°C.

12. A film according to claim 11, wherein said differential is at least 25°C.

13. A film according to claim 12, wherein said differential is at least 40°C.

14. A film according to any one of claims 5 to 13, wherein the outermost layer comprises polyethylene terephthalate, polypropylene, polycarbonate, or high density polyethylene.

15. A film according to any preceding claim, wherein the product-contacting and outermost layers include antiblock and slip compounds.

16. A product according to claim 15, wherein said compounds comprise silica and erucamide acid.

17. A film according to any preceding claim, wherein at least one of said intermediate layer and said product-contacting layer comprises at least one highly flexible polymer.

18. A film according to claim 17, wherein said highly flexible polymer comprises impact-modified polypropylene; low density polyethylene; low density polyethylene produced by using a metallocene catalyst system; very low density, linear low density polyethylene; polyolefin plastomer; or polyamide with a low degree of crystallinity.

19. A film according to claim 18, wherein said impact-modified polypropylene has been produced using a metallocene-type catalyst system.

20. A film according to claim 18 or 19, wherein said very low density, linear low density polyethylene has been polymerized using a Ziegler Natta catalyst system and, after polymerization, grafted with maleic acid anhydride.

21. A film according to claim 18, 19, or 20, wherein said

polyolefin plastomer has been produced by using a metallocene catalyst system.

22. A film according to any one of claims 18 to 21, wherein said polyamide with a low degree of crystallinity is a copolyamide.

23. A film according to claim 22, wherein said copolyamide has been copolymerized by condensation polymerization of a diamine and a dicarbonic acid.

24. A film according to any preceding claim, wherein said product-contacting layer comprises at least one high-performance resin with a very low level of short molecular weight fractions and an ultra low level of non-polymerized monomers.

25. A film according to claim 24 as appended to claim 10, wherein said at least one high-performance resin comprises low softening point, flexible polyolefin.

26. A film according to claim 25, wherein said low softening point, flexible polyolefin comprises at least one of low density polyethylene; linear low density polyethylene produced by using a metallocene catalyst system; and polyolefin plastomer produced by using a metallocene catalyst system.

27. A film according to any preceding claim, wherein at least one of the intermediate layer and the product-contacting layer has a higher light barrier property than the outermost layer.

28. A film according to claim 27, and containing an innermost light barrier and an outermost light barrier which are light in colour and at least one intermediate light barrier which is dark in colour.

29. A film according to any preceding claim and in the form of at least a section of a collapsed, multi-layer tube whereof the innermost layer is in a condition thermo-laminated to itself.

30. A film according to claim 29, wherein said innermost layer comprises polyolefin plastomer, ethylene vinyl acetate,

ethylene metacrylic acid, ethylene acrylic acid, an ionomer, or polyamide co-polymer with a melting point no higher than about 160°C.

31. A film according to any preceding claim, and further comprising at least one further intermediate layer having gas barrier properties.

32. A film according to claim 31, wherein said at least one further intermediate layer comprises at least one of aluminium, aluminium oxide, silicon oxide, melamine, diamond-like carbon, and polymers.

33. A film according to any preceding claim, wherein at least the intermediate layer(s) and the product-contacting layer have been co-extruded.

34. A film according to claim 33, wherein the outermost layer has been manufactured by extrusion and forms a first sub-film which is laminated to the other layers of the film, which are in the form of a second sub-film.

35. A film according to any preceding claim, wherein said outermost layer comprises a rubber-modified plastics.

36. A multi-layer packaging pouch comprising, progressing towards a surface of the pouch contacting an aqueous product packaged therein, an outermost layer, an intermediate layer, and a product-contacting layer, said outermost layer having a higher softening point than said product-contacting layer, and said intermediate layer comprising a material having a higher drop strength than the material of said outermost layer.

37. A pouch according to claim 36, wherein said intermediate layer comprises at least one highly flexible polymer.

38. A pouch according to claim 37, wherein said highly flexible polymer comprises impact-modified polypropylene; low density polyethylene; low density polyethylene produced by using a metallocene catalyst system; very low density, linear low density polyethylene; polyolefin plastomer; or polyamide with a low degree of crystallinity.

39. A pouch according to claim 38, wherein said

polypropylene has been produced using a metallocene-type catalyst system.

40. A pouch according to claim 38 or 39, wherein said very low density, linear low density polyethylene has been polymerized using a Ziegler Natta catalyst system and, after polymerization, grafted with maleic acid anhydride.

41. A pouch according to claim 38, 39, or 40, wherein said polyolefin plastomer has been produced by using a metallocene catalyst system.

42. A pouch according to any one of claims 38 to 41, wherein said polyamide with a low degree of crystallinity is a copolyamide.

43. A pouch according to claim 42, wherein said copolyamide has been copolymerized by condensation polymerization of a diamine and a dicarbonic acid.

44. A pouch according to any one of claims 36 to 43, wherein at least one of the outermost layer and the intermediate layer is of a material stiffer than that of the product-contacting layer.

45. A pouch according to claim 44, wherein said material stiffer than that of the product-contacting layer comprises a stiff, extrudable polymer.

46. A pouch according to claim 45, wherein said material stiffer than that of the product-contacting layer comprises polyester, polypropylene, polycarbonate, or high density polyethylene.

47. A pouch according to claim 46, wherein said polyester comprises polyethylene terephthalate.

48. A pouch according to claim 46 or 47, wherein said polypropylene comprises crystalline polypropylene.

49. A pouch according to any one of claims 36 to 48, wherein the outermost layer has a higher softening point than the product-contacting layer.

50. A pouch according to claim 49, wherein the outermost layer and the product-contacting layer have a melting point differential of at least 15°C.

51. A pouch according to claim 50, wherein said differential

is at least 25°C.

52. A pouch according to claim 51, wherein said differential is at least 40°C.

53. A pouch according to any one of claims 44 to 52, wherein the outermost layer comprises polyethylene terephthalate, polypropylene, polycarbonate, or high density polyethylene.

54. A pouch according to any one of claims 36 to 53, wherein the product-contacting and outermost layers include antiblock and slip compounds.

55. A pouch according to claim 54, wherein said compounds comprise silica and erucamide acid.

56. A pouch according to any one of claims 36 to 55, wherein said product-contacting layer comprises at least one high-performance resin with a very low level of short molecular weight fractions and an ultra low level of non-polymerized monomers.

57. A pouch according to claim 56 as appended to claim 49, wherein said at least one high-performance resin comprises low softening point, flexible polyolefin.

58. A pouch according to claim 57, wherein said low softening point, flexible polyolefin comprises at least one of low density polyethylene; linear low density polyethylene produced by using a metallocene catalyst system; and polyolefin plastomer produced by using a metallocene catalyst system.

59. A pouch according to any one of claims 36 to 58, wherein the product-contacting layer has a higher light barrier property than the outermost layer.

60. A pouch according to claim 59, wherein the wall of said pouch contains an innermost light barrier and an outermost light barrier which are light in colour and at least one intermediate light barrier which is dark in colour.

61. A pouch according to any one of claims 36 to 60 and having its wall in the form of at least a section of a collapsed, multi-layer tube whereof the innermost layer is in a condition thermo-laminated to itself.

62. A pouch according to claim 61, wherein said innermost layer comprises polyolefin plastomer, ethylene vinyl acetate, ethylene metacrylic acid, ethylene acrylic acid, an ionomer, or polyamide co-polymer with a melting point no higher than about 160°C.

63. A pouch according to any one of claims 36 to 61, and further comprising at least one further intermediate layer having gas barrier properties.

64. A pouch according to claim 63, wherein said at least one further intermediate layer comprises at least one of aluminium, aluminium oxide, silicon oxide, melamine, diamond-like carbon, and polymers.

65. A pouch according to any one of claims 36 to 64, wherein at least the intermediate layer(s) and the product-contacting layer have been co-extruded.

66. A pouch according to claim 65, wherein the outermost layer has been manufactured by extrusion and forms a first sub-film which is laminated to the other layers of the film which are in the form of a second sub-film.

67. A pouch according to any preceding claim, wherein said outermost layer comprises a rubber-modified plastics.

68. A multi-layer film comprising:-

a first layer comprised of any of the group consisting of PET, PP, PC and HDPE,

a second layer comprised of a sealing polymer,

between said first layer and said second layer, third and fourth layers of which the third layer is nearer to said first layer than is said fourth layer,

light-coloured pigment in said third layer,

dark-coloured pigment in said fourth layer, and

light-coloured pigment in said film and located between said dark-coloured pigment and that surface of said film further from said first layer.

69. A film according to claim 68, wherein the sealing polymer has been produced using a metallocene catalyst.

70. A film according to claim 68 or 69, wherein the first

layer and the second layer have a melting point differential of at least 15°C.

71. A film according to claim 70, wherein said differential is at least 25°C.

72. A film according to claim 71, wherein said differential is at least 40°C.

73. A film according to any one of claims 68 to 72, wherein the first layer comprises polyethylene terephthalate, polypropylene, polycarbonate, or high density polyethylene.

74. A film according to any one of claims 68 to 73, wherein the first and second layers include antiblock and slip compounds.

75. A film according to claim 74, wherein said compounds comprise silica and erucamide acid.

76. A film according to any one of claims 68 to 75, wherein at least one of the first, third and fourth layers is of a material stiffer than that of the second layer.

77. A film according to claim 76, wherein said material stiffer than that of the second layer comprises a stiff, extrudable polymer.

78. A film according to claim 77, wherein said material stiffer than that of the second layer comprises polyester, polypropylene, polycarbonate, or high density polyethylene.

79. A film according to claim 78, wherein said polyester comprises polyethylene terephthalate.

80. A film according to claim 78 or 79, wherein said polypropylene comprises crystalline polypropylene.

81. A film according to any one of claims 68 to 80, wherein said second layer comprises at least one high-performance resin with a very low level of short molecular weight fractions and an ultra low level of non-polymerized monomers.

82. A film according to claim 81, wherein said at least one high-performance resin comprises low softening point, flexible polyolefin.

83. A film according to claim 82, wherein said low softening point, flexible polyolefin comprises at least one of low

density polyethylene; linear low density polyethylene produced by using a metallocene catalyst system; and polyolefin plastomer produced by using a metallocene catalyst system.

84. A film according to any one of claims 68 to 83 and in the form of at least a section of a collapsed, multi-layer tube whereof the innermost layer is in a condition thermo-laminated to itself.

85. A film according to claim 84, wherein said innermost layer comprises polyolefin plastomer, ethylene vinyl acetate, ethylene metacrylic acid, ethylene acrylic acid, an ionomer, or polyamide co-polymer with a melting point no higher than about 160°C.

86. A film according to any one of claims 68 to 84, wherein at least one of said third and fourth layers has gas barrier properties.

87. A film according to claim 86, wherein said at least one of said third and fourth layers comprises at least one of aluminium, aluminium oxide, silicon oxide, melamine, diamond-like carbon, and polymers.

88. A film according to any preceding claim, wherein at least the second, third and fourth layers have been co-extruded.

89. A film according to claim 88, wherein the first layer has been manufactured by extrusion and forms a first sub-film which is laminated to the other layers of the film which are in the form of a second sub-film.

90. A film according to any one of claims 68 to 89, wherein said first layer comprises a rubber-modified plastics.

91. A method of producing a laminate by collapsed bubble extrusion, comprising extruding a multi-layer tube including a light-barrier substance, and collapsing the tube and thermo-laminating the innermost layer of the tube to itself.

92. A method according to claim 91, and followed by forming a section of said laminate into a container.

93. A method according to claim 92, wherein said forming of the section of said laminate comprises bringing and sealing together opposite edge zones of said section to give said section a tubular form, sealingly closing a lower end of the tubular-form section, filling the tubular-form section with a product, and then sealingly closing an upper end of the tubular-form section.

94. A method according to claim 92 or 93, wherein said container is a pouch.

95. A laminate in the form of a collapsed, multi-layer tube which includes a light-barrier substance and whereof the innermost layer is in a condition thermo-laminated to itself.

96. A laminate according to claim 95, wherein said innermost layer comprises polyolefin plastomer, ethylene vinyl acetate, ethylene metacrylic acid, ethylene acrylic acid, an ionomer, or polyamide co-polymer with a melting point no higher than about 160°C.

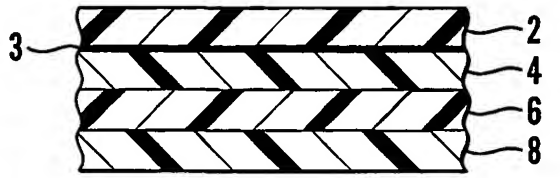

Fig.1

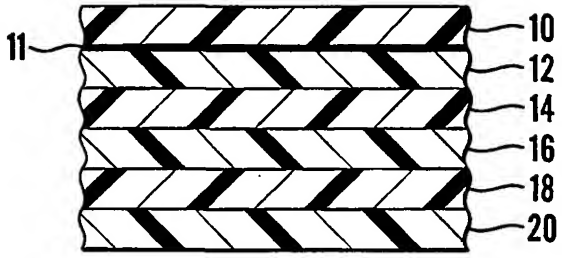

Fig.2

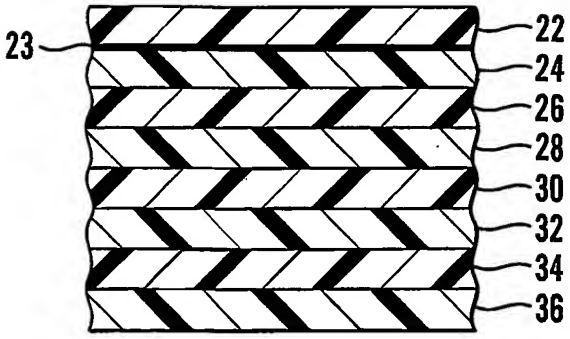

Fig.3

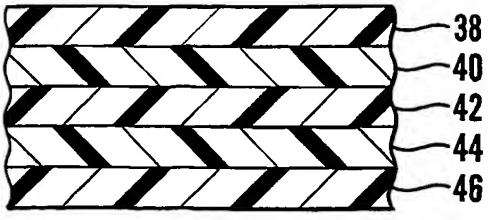

Fig.4

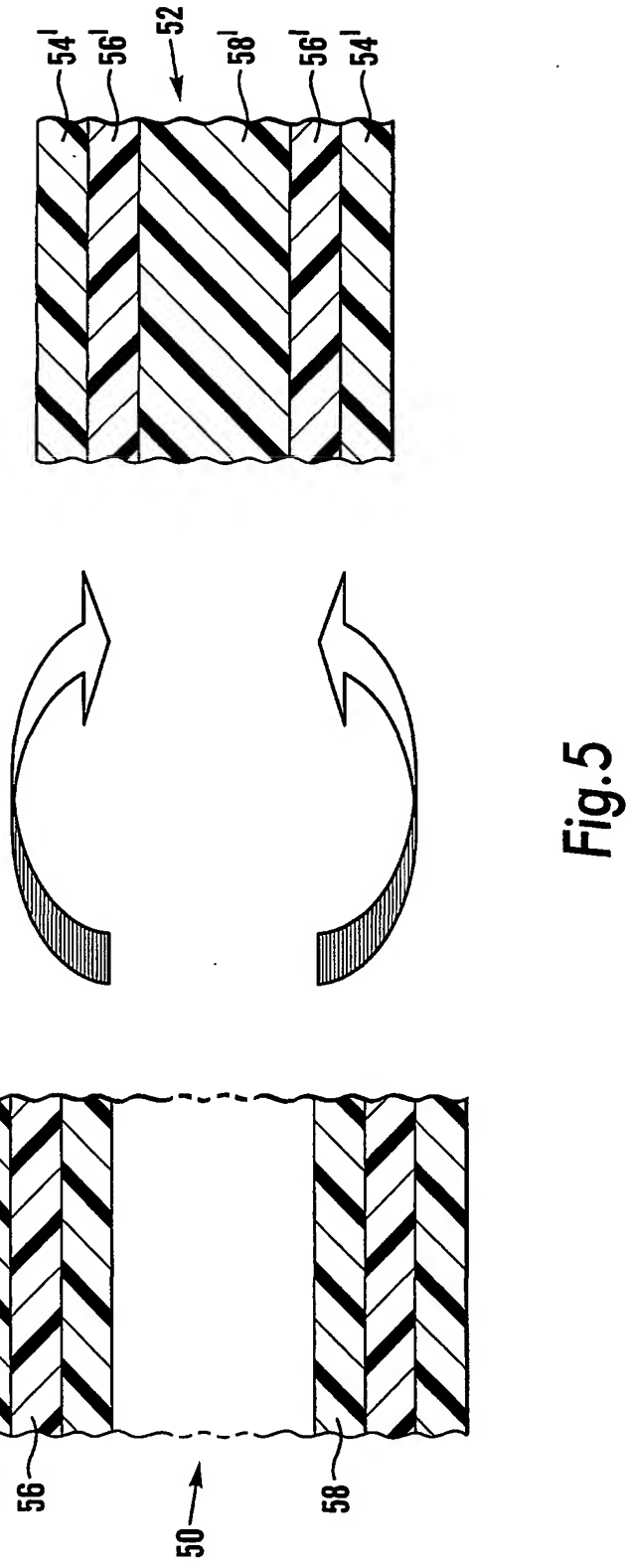

Fig.5

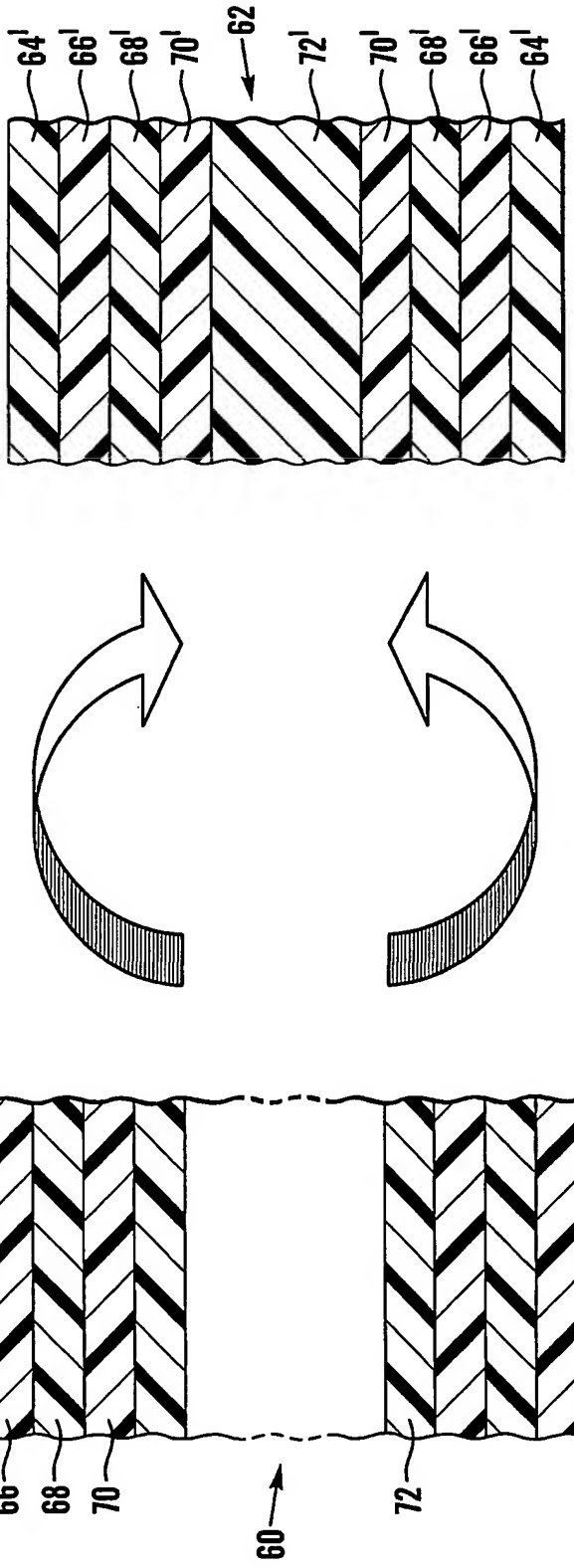

Fig.6

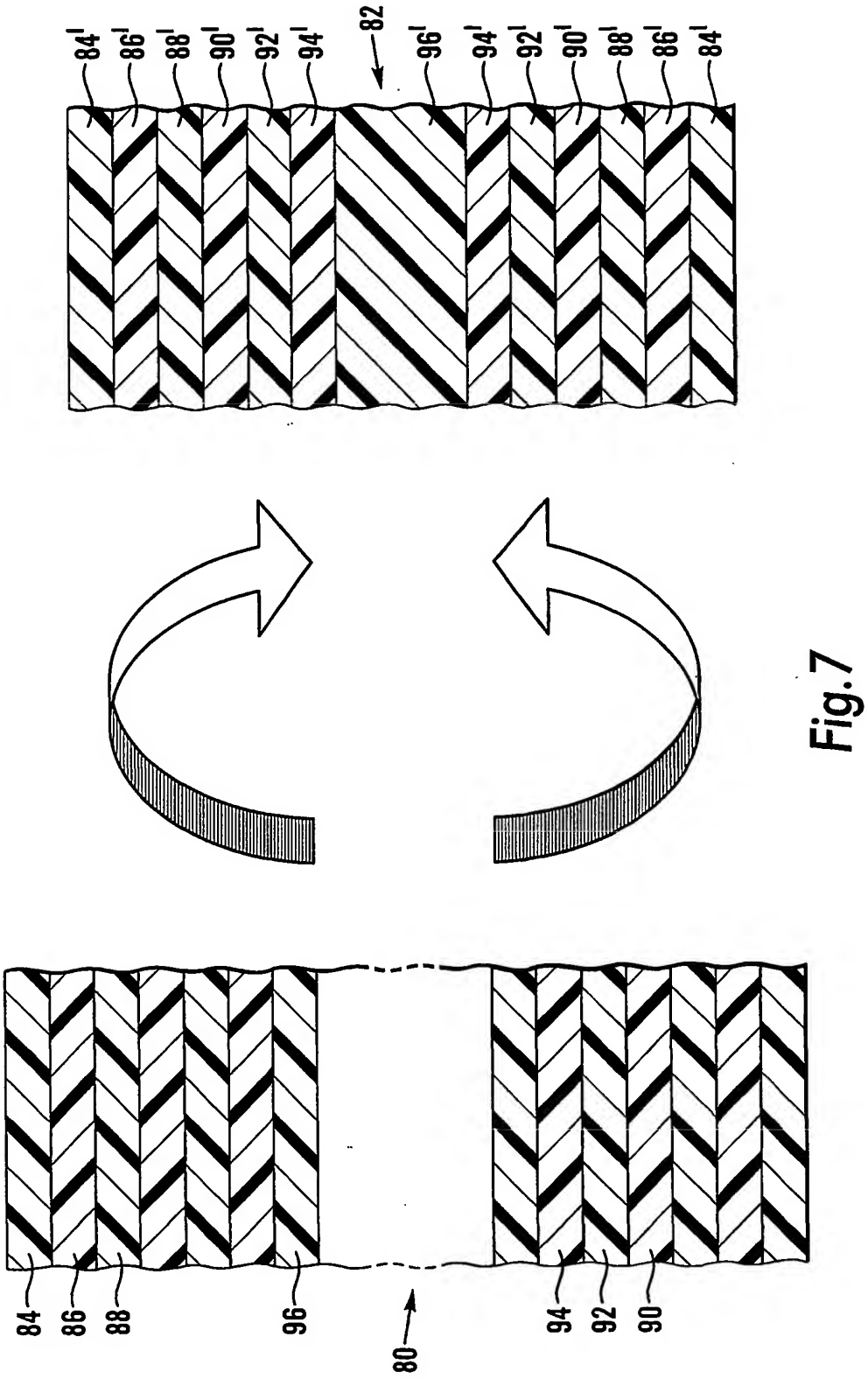

Fig.7